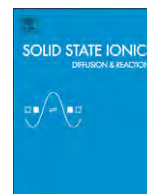




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# The role of Al and Li concentration on the formation of cubic garnet solid electrolyte of nominal composition $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

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## ABSTRACT

The effect of Al and Li concentration on the formation of cubic garnet of nominal composition  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  was investigated. It was determined that at least 0.204 moles of Al is required to stabilize the cubic phase. It was observed for the cubic phase (stabilized by the addition of Al) that as Li content was increased from 6 to 7 moles it transformed to a tetragonal phase. Additionally, powders of cubic  $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$  were hot-pressed at 1000 °C and 40 MPa. The hot-pressed material had a relative density of 98%. The room temperature total ionic conductivity of the hot-pressed material was  $4.0 \times 10^{-4}$  S/cm and the electronic conductivity was  $2 \times 10^{-8}$  S/cm.

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## 1. Introduction

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) has recently become of high interest as a result of its potential as a solid state Li-ion conductor, because it has good ionic conductivity ( $>10^{-4}$  S/cm) and is stable against lithium [1–8]. However, for the case of LLZO two phases exist; cubic and tetragonal [1–9]. The cubic phase is preferred, because reports estimate a theoretical lattice conductivity of  $\sim 5 \times 10^{-4}$  S/cm [1,6] compared to  $\sim 1.6 \times 10^{-6}$  S/cm [9], for the tetragonal phase. Thus, it is important to understand how to prepare the cubic phase.

Several reports describe the synthesis and characterization of LLZO using solid state reactions [2,4–6,9] and wet chemical techniques [1,3]. A summary of the techniques, processing variables (temperature and chemical composition) and resulting phase(s) are listed in Table 1. From Table 1 it is seen that there are several parameters that determine whether cubic or tetragonal LLZO forms. The calcination temperature, ostensibly, appears to be the most critical parameter. In general, calcination temperatures in excess of 1180 °C are required to obtain cubic LLZO. As a result of the high calcination temperature two variables come into play, the first is Al contamination from  $\text{Al}_2\text{O}_3$  crucibles. From Table 1 it is observed that for cubic LLZO calcined at high temperatures, several groups have reported the presence of small

concentrations of Al. It should be noted that for the case of Geiger et al. [4] and Shimonishi et al. [1] no Al was in the starting precursors. They suggest that the Al in LLZO came from a reaction at the high temperatures with the  $\text{Al}_2\text{O}_3$  crucibles. For the case of Kumazaki et al. [5] they intentionally used  $\text{Al}_2\text{O}_3$  crucibles to react with LLZO pellets to get Al into the pellets. Geiger et al. [4], Shimonishi et al. [1] and Kumazaki et al. [5] obtained cubic LLZO with confirmed Al molar concentrations of 0.19, 0.23 and 0.40, respectively. Kumazaki et al. [5] reported that at Al molar concentrations between 0.074 and 0.1, tetragonal LLZO formed. These reports suggest that a critical concentration of Al may be required to stabilize cubic LLZO.

The second variable, which can be influenced by high temperature calcination, is Li content. In general, calcination temperatures below 1180 °C result in tetragonal LLZO. It has been reported that the measured concentration of Li in cubic LLZO is significantly less than in tetragonal LLZO [1, 4]. For example, both Shimonishi et al. [1] and Geiger et al. [4] obtain cubic LLZO at Li concentrations of 5.96 (calcined at 1180 °C) and 6.27 (calcined at 1230 °C) moles, respectively. In the case of Shimonishi et al. [1], the Li concentration of approximately 6.0 moles Li was observed for cubic LLZO despite the fact that up to 2.0 moles of excess Li was used in the precursor powders. Conversely, Shimonishi et al. [1] observed in samples calcined at 800 °C, where no significant amounts of Li loss occurred, that tetragonal LLZO formed at Li concentrations of 7 and 7.5 moles.

From the above, it is apparent that the phase stability of cubic LLZO is influenced by the Al and Li concentration. However, there has been no detailed study to determine these effects. To this end,

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**Table 1**  
Synthesis and structure of nominal composition  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ .

Synthesis technique	Temperature (°C)	Al (moles) <sup>a</sup>	Li (moles) <sup>a</sup>	Tetragonal	Cubic
Pechini [3]	700				X
Pechini [3]	800			X	
Pechini [1]	800	–	7.0, 7.5	X	
Pechini [3]	900			X	
Pechini [1]	1180	0.23	5.96		X
Solid state [2, 9]	900			X	
Solid state [9]	980			X	
Solid state [2]	1125			X	
Solid state [8]	1200				X
Solid state [5]	1230	0.074–0.15	–	X	
Solid state [4]	1230	0.19	6.27		X
Solid state [5]	1230	0.40	–		X
Solid state [2]	1230				X
Solid state [6]	1230				X

<sup>a</sup> Confirmed by ICP.

we conducted a systematic study involving the deliberate and precise addition of Al and Li to LLZO and evaluated the structure using x-ray diffraction (XRD) and chemical composition using inductively coupled plasma (ICP) analysis.

In addition, once the critical amount of Al and Li was determined it was decided to use this information to prepare powders of cubic LLZO and consolidate them using uniaxial hot-pressing to determine the ionic and electronic properties of a dense pellet and compare to values determined using conventional sintering.

## 2. Experimental

### 2.1. Sample synthesis

Lithium Carbonate (Puratronic 99.998% Alfa Aesar), Lanthanum (III) Hydroxide (99.95% Alfa Aesar), Zirconium Oxide (99.9% Inframatt Advanced Materials LLC) and Aluminum Oxide (50 nm Gamma “B” from Mager Scientific Inc) precursors used to form LLZO of various Al and Li concentrations. They were added into an agate milling vial for mixing. A Retsch PM-100 planetary mill with agate milling media was used to mix the precursors. After mixing the powders were collected and cold pressed into pellets. The pellets were placed in boron nitride coated  $\text{Al}_2\text{O}_3$  combustion boats (Coors Combustion boat from Sigma Aldrich) and fired in air at 1000 °C for 4 h. The boron nitride (BN) coating was used to prevent the  $\text{Al}_2\text{O}_3$  crucible from reacting with the pellets.

### 2.2. Material characterization

To determine the phases present after heat-treatment XRD (Bruker AXS D8 Advance with Da Vinci) was conducted using copper  $K_\alpha$  radiation. To determine the concentration of cations, ICP was conducted by Galbraith Laboratories (Tennessee, USA).

### 2.3. Hot-pressed sample preparation

A 22 mm diameter, 2 mm thick pellet of cubic LLZO pellet (with the composition  $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$ ) was prepared by loading single phase powder into a graphite die and heating at 1000 °C under 40 MPa pressure for 1 h under flowing argon. The resulting pellet was removed from the hot press and heated in air at 1000 °C for 4 h to burn off residual graphite from the hot pressing die. After burning off the graphite residue, the pellet appeared bright white and was mounted in crystalbond wax and cut into multiple parallelepipeds using a diamond saw for characterization.

### 2.4. Hot-pressed sample characterization

AC and DC room temperature electrical conductivity measurements were performed on the hot-pressed sample using the two probe method. Au was sputter coated on to the top and bottom surfaces of the specimens. AC measurements were undertaken to determine ionic conductivity. AC impedance was measured using a Solatron 1260 Impedance Analyzer in the frequency range 1 to  $10^6$  Hz. DC measurements were undertaken to determine electronic conductivity. DC resistances were measured using a Keithley 6517A Electrometer/High Resistance Meter with a Model 8009 Resistivity Test Fixture capable of measuring volume resistivities as high as  $10^{18}$  ohms-cm. The microstructure of the hot-pressed sample was examined on a fracture surface using scanning electron microscopy (JEOL JSM-7500F, SEM). Thin-foil TEM specimens were prepared from rectangular parallelepipeds using conventional mechanical and ion milling techniques to produce an electron transparent region using a series of diamond lapping films and a precision ion polishing system (Fischione Ion Mill model 1010) at low temperature (–60 °C) with a finishing accelerating voltage of 0.5 kV. The microstructure of specimen was examined using TEM (JEOL 2100F field-emission with Scanning Transmission Electron Microscope (STEM) capability and Oxford EDS system) operated at 200 kV. Micro-chemical analysis was examined using EDS system along with STEM mode.

## 3. Results and discussion

### 3.1. Effect of Al on the formation of cubic LLZO at a fixed Li concentration

A series of experiments was conducted to evaluate the effect of Al on the formation of cubic LLZO. To eliminate Li concentration as a variable, the Li precursor composition was fixed at 7 moles Li. This is similar to the Li precursor composition used by Geiger et al. [4] and Shimonishi et al. [1]. ICP analysis later revealed that the actual Li content of the powders after calcination was 6.24 moles, which is similar to the actual Li amount observed by Geiger et al. [4] and Shimonishi et al. [1]. ICP data also confirmed that the BN coating prevented reactions with the  $\text{Al}_2\text{O}_3$  crucible. For example, the sample that did not have any intentionally added Al did not contain Al. Similarly, the sample in which 0.24 moles of Al was intentionally added, precisely contained 0.24 moles. From this, it can be concluded that whatever Al that was present in the samples was only the intentionally added Al. 0.000 and 0.093 to 0.389 moles of Al, in 0.037 mole increments, was added to the LLZO precursors and calcined at 1000 °C in air for 4 h. The range of Al that was selected was more or less centered upon the concentrations of 0.19 and 0.23 moles Al that was reported by Geiger et al. [4] and Shimonishi et al. [1], respectively. Fig. 1 is the XRD data as a function of Al content. XRD analysis shows a transformation from tetragonal to cubic LLZO with increasing Al content, reaching a critical concentration for the formation of the cubic phase at or above 0.204 moles of Al (Fig. 1), which is in excellent agreement with the results of Geiger et al. [4]. The tetragonal phase can be identified by peak doublets; the most pronounced is centered at  $2\theta = 30.5$  degrees (see box in Fig. 1). At or above 0.204 moles Al, the peak doublet centered at  $2\theta = 30.5$  degrees merges into one well defined peak giving rise to phase pure cubic LLZO. At the highest Al concentration of 0.389 moles, two phases exist, cubic LLZO and  $\text{LaAlO}_3$ . It is believed that at this Al concentration the solubility limit of Al in cubic LLZO is exceeded and second phase  $\text{LaAlO}_3$  forms. This is in reasonably good agreement with the XRD data of Kumazaki et al. [5], which shows evidence of second phase  $\text{LaAlO}_3$  along with cubic LLZO at 0.40 moles of Al.

From the above analysis it is apparent that, in relatively small quantities, Al plays a critical role in stabilizing the formation of cubic LLZO. At present the exact role that Al plays is in stabilization of the cubic phase is not well understood. Geiger et al. [4] has

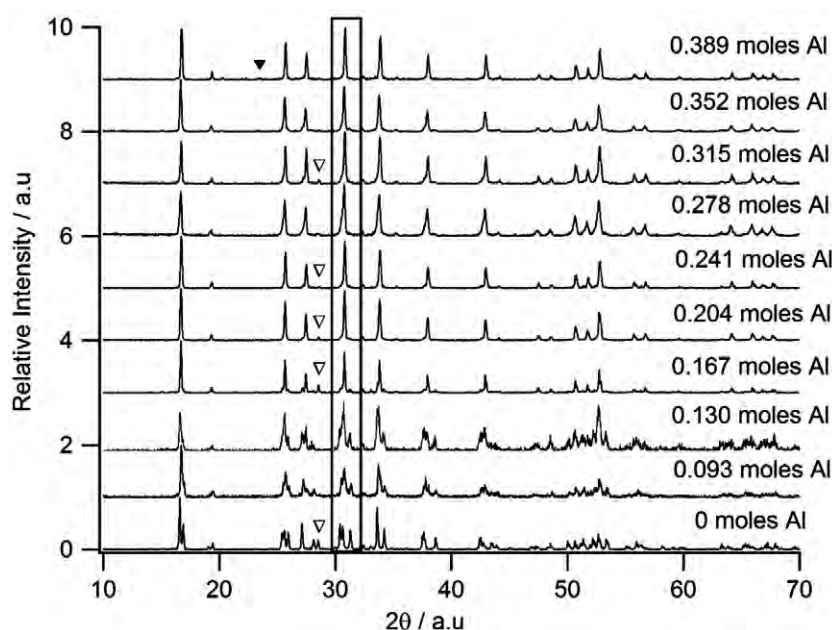


Fig. 1. XRD patterns of the nominal composition  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  calcined at  $1000^\circ\text{C}$  in air for 4 h with Li fixed at 7.0 in the precursor powders:  $\blacktriangledown\text{Al}_2\text{O}_3$ ,  $\triangledown\text{La}_2\text{Zr}_2\text{O}_7$ .

suggested that Al substitutes for Li and that this substitution may act to stabilize the cubic phase relative to the tetragonal phase. However, a detailed mechanism was not proposed. It is possible that stabilization of the cubic phase could be related to the size (cationic radius) and charge of the Al dopant. In the case of charge, since  $\text{Al}^{3+}$  substitutes for three  $\text{Li}^+$  cations, two Li vacancies are formed according to the charge neutrality condition below (Kroger–Vink notation):

$$2[\text{Al}_{\text{Li}}^{\bullet}] = [\text{V}_{\text{Li}}'] \quad (1)$$

It is possible that it is the Li vacancy concentration which determines phase stability, similar to that suggested for the case of oxygen vacancies in aliovalent cation doped  $\text{ZrO}_2$  [10–13]. For example, at Al concentrations  $< 0.204$  moles, the Li vacancy concentration is below a critical value; in which case tetragonal LLZO forms and above this value cubic LLZO forms. It should be noted that the cubic structure has higher conductivity which may be related not only to the difference in structures but also to the difference in Li vacancy concentration between the cubic and tetragonal phases. If this theory is correct then, it is expected that other aliovalent dopants which substitute for Li with the appropriate radius may also stabilize the cubic phase. In any case, more detailed work is needed to determine the exact role of Al on the phase stability in LLZO.

### 3.2. Effect of Li on the formation of cubic LLZO at fixed Al concentration

A series of experiments was conducted to evaluate the effect of Li concentration on the formation of cubic LLZO. As was made evident in Section 3.1, cubic LLZO is stabilized by the addition of Al at or above 0.204 moles. Thus, in this study the Al concentration was fixed at 0.240 moles. Samples were made with varying amounts of Li (where  $x$  = moles Li in the precursors in the nominal formula  $\text{Li}_{8-x}\text{Li}_{0.48}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{12.62-x/2}$ ).  $x$  varied between 0.0 and 2.0 in 1.0 mole increments. Since it has been shown that Li loss occurred during calcination [1,4], the three compositions were analyzed for Li content by ICP after calcination at  $1000^\circ\text{C}$ . ICP confirmed that there was Li loss after heating at  $1000^\circ\text{C}$ . ICP analysis revealed that the measured Li molar concentrations were 5.63, 6.24 and 7.32 for the samples in which the intended molar concentrations were 6.0, 7.0 and 8.0 moles, respectively. Measuring the oxygen content was attempted with a pyrolysis technique, however, due to

the relatively high metal content the oxygen content could not be verified. Thus, the oxygen content, in the proposed composition  $\text{Li}_{8-x}\text{Li}_{0.48}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{12.62-x/2}$  was implied based on maintaining charge neutrality assuming the Al doping effect described in Eq. (1).

Fig. 2 is the XRD data as a function of Li content. From Fig. 2 several important points are noted. Firstly, at  $x = 5.63$  (measured Li content) cubic LLZO is present (as was made evident by the lack of peak splitting at  $2\theta = 30.5$  degrees; see box in Fig. 2) along with second phase  $\text{La}_2\text{Zr}_2\text{O}_7$ . Thus, at this Li concentration there is insufficient Li to form single phase cubic LLZO and some  $\text{La}_2\text{Zr}_2\text{O}_7$  formed as a result. This may suggest a lower limit to the Li concentration required to form single phase cubic LLZO.

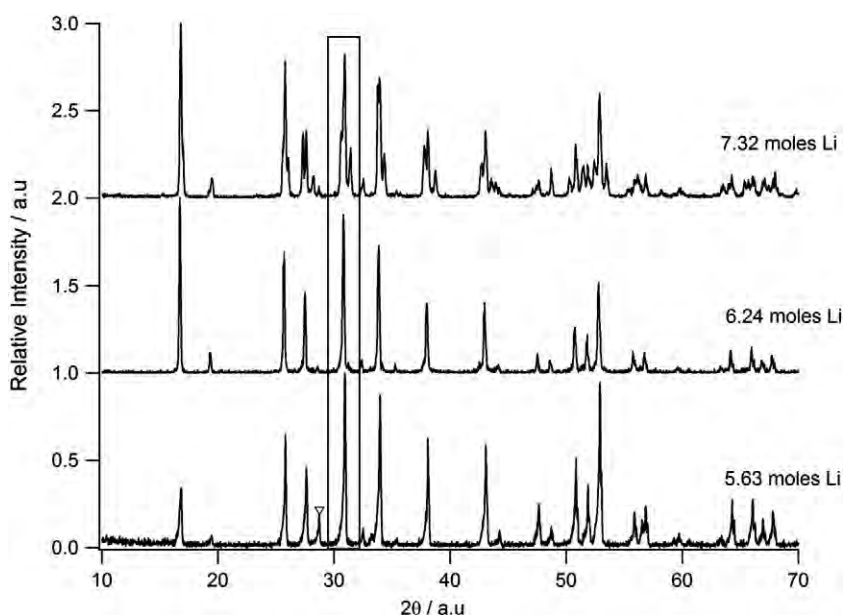
Secondly, XRD analysis shows going from  $x = 5.63$  to 6.24 that  $\text{La}_2\text{Zr}_2\text{O}_7$  phase does not form and only single phase cubic LLZO is present, as is evident from the lack of peak splitting at  $2\theta = 30.5$  degrees (see box in Fig. 2). The concentrations of Li and Al required to obtain cubic LLZO is in good agreement with the values reported in Table 1. Thirdly, that as the Li content increases from 6.24 to 7.32 moles a transformation from cubic to tetragonal LLZO occurs. This is evident from the peak splitting at  $2\theta = 30.5$  degrees (see box in Fig. 2). This suggests that, despite having Al present, there is an upper limit to the Li concentration at which the cubic phase is not stable. Based on Fig. 2 it is speculated that this limit is between 6 and 7 moles of Li.

At present, reasons for the transition from cubic to tetragonal LLZO as the Li content increases are not known. However it is possible that the addition of Li above the critical Li concentration fills specific Li vacancy sites to the degree that one or more of the unit cell axes must distort to accommodate the further uptake of Li. More detailed work is needed to determine the exact role of Li in this transition. In any case, the above results showed that Li concentration plays a role in the formation of cubic LLZO despite having enough Al to stabilize the cubic phase. Since, both Al and Li concentration play a critical role in the formation of cubic LLZO, further work is required to determine how the ratio of Li to Al can be optimized to maximize ionic conductivity.

### 3.3. Characterization of hot-pressed cubic LLZO

The optimum concentration of Al (0.24 moles) to form cubic LLZO from Section 3.1 and optimum concentration of Li (6.24 moles) to form cubic LLZO from Section 3.2 were selected for the fabrication of a





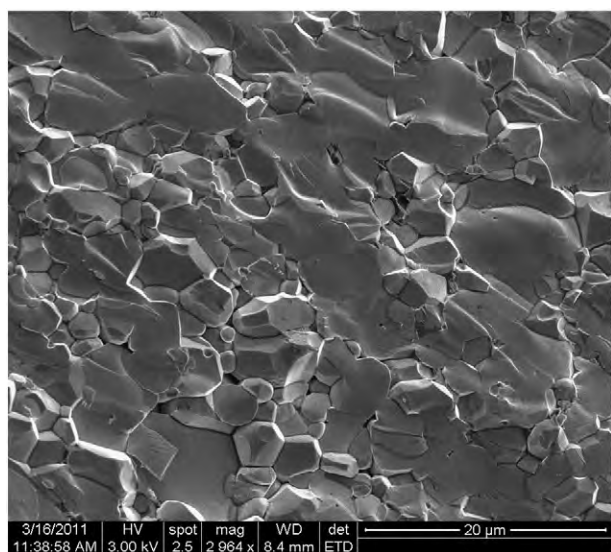
**Fig. 2.** XRD patterns of  $\text{Li}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  where the precursor value of “x” was varied from 6.0 to 8.0 moles Li with Al fixed at 0.24 moles. Each XRD pattern is labeled with the corresponding ICP verified Li concentrations after calcination. Samples were calcined at 1000 °C in air for 4 h;  $\nabla \text{La}_2\text{Zr}_2\text{O}_7$ .

hot-pressed LLZO pellet of exact composition,  $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$ . The cation composition was measured by ICP and the oxygen concentration was estimated to maintain charge neutrality. Although not shown, XRD confirmed that after hot-pressing the pellet was single-phase cubic LLZO. The density of the hot-pressed pellet was determined from the weight and physical dimensions. The relative density of the hot-pressed material was 98%. An SEM micrograph of the hot-pressed sample's fracture surface is shown in Fig. 3. From Fig. 3 several important points are noted. Firstly, the sample is very dense, in agreement with the high relative density, very few voids are observed. Secondly, the fracture is mainly transgranular, indicating high grain boundary strength. Thirdly, the average grain size is around 4  $\mu\text{m}$ .

The room temperature AC conductivity results for the hot-pressed cubic LLZO sample using Li-ion blocking Au electrodes are shown in Fig. 4. From Fig. 4 several important points are noted. Firstly, no clear semicircles are observed. Only a vertical “tail” at low frequencies is observed. Since Li-ion blocking electrodes were used, this tail

indicates a predominately ionic conductor [14,15]. The shape of the curve shown in Fig. 4 is in good agreement with the results of Kotobuki et al. [2] and Kumazaki et al. [5] for cubic LLZO. Kotobuki et al. [2] suggested that the lack of clear semicircles at the highest frequencies may imply that grain boundary impedance is negligible compared to lattice impedance. Kumazaki et al. [5] suggested that the lack of a clear semicircle in the highest conductivity sample was a result that the grain boundary resistance was almost removed in this sample. This is reasonable in our case since, we have almost a fully dense sample and Murugan et al. [6] reveal that for cubic LLZO that the grain boundary and lattice conductivities are of the same order of magnitude. Secondly, using the low frequency intercept on the  $Z'$  axis and the sample dimensions yields a total ionic conductivity value of  $4 \times 10^{-4}$  S/cm. The value of  $4 \times 10^{-4}$  S/cm is one of the highest total ionic conductivity values for cubic LLZO containing only Al with no other intentional additives. Previous values for total ionic conductivity for cubic LLZO containing only Al range from 1.4 to  $2.5 \times 10^{-4}$  S/cm. [1,2,5–8]. The electronic conductivity of the hot-pressed sample is  $2 \times 10^{-8}$  S/cm. Using this value in conjunction with the total ionic conductivity value yields an ionic transport number (ionic conductivity/total conductivity) equal to 1.0, confirming that cubic LLZO is an ionic conductor.

The total conductivity of hot-pressed cubic LLZO as a function of temperature is shown in Fig. 4b. From Fig. 4b the activation energy for the total conductivity determined from the slope of the curve is 0.26 eV. This activation energy value is about 13% lower than the value determined by Murugan et al. [6] of 0.30 eV and about 30% lower than the value determined by Shimonishi et al. [1] of 0.37 eV. At present the exact reason(s) for the difference in activation energy between the various studies are not known. It is believed that the consolidation step is one of the major variables that could lead to the lower activation energy observed for the present study compared to those observed by Murugan et al. [6] and Shimonishi et al. [1]. In the present study the material was consolidated by hot-pressing at 1000 °C at shorter times compared to conventional sintering at  $\geq 1180$  °C for Shimonishi et al. [1] and Murugan et al. [6]. The lower temperature and shorter times likely results in lower lithium loss at the grain boundaries. Lower lithium loss should result in higher conductivity grain boundaries as suggested by Ban et al. [16] and hence, a lower activation energy. TEM images (Fig. 5) indicate the grain boundaries are relatively thin ( $\sim 2$  nm) and free of voids, thus



**Fig. 3.** SEM image of a fracture surface of hot-pressed  $\text{Li}_{6.24}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{11.98}$ .

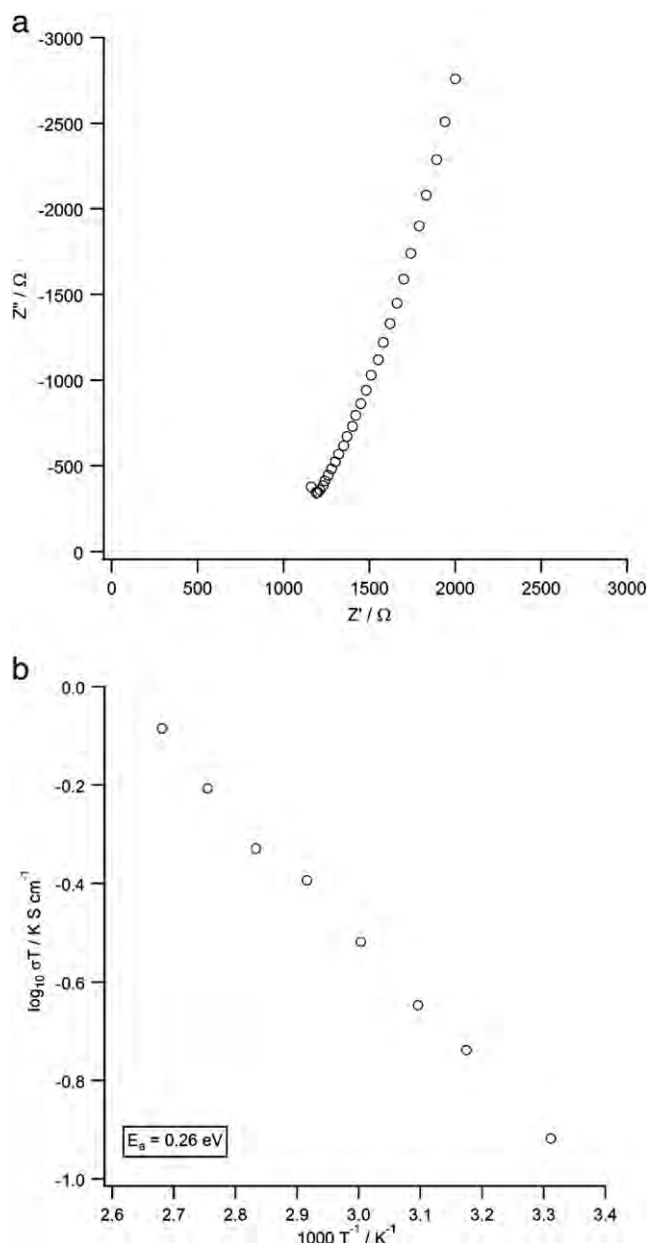


Fig. 4. Hot pressed pellet ( $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}$ ) ionic conductivity data. Complex impedance (a), Arrhenius plot (b).

facilitating transgranular conductivity. Additionally, no amorphous phases were detected at triple junctions or along grain boundaries.

#### 4. Conclusions

The effect of Al and Li concentration on the formation of nominal composition  $Li_7La_3Zr_2O_{12}$  was investigated. It was determined that at least 0.204 moles of Al is required to stabilize the cubic phase. Below this Al content the tetragonal phase exists. As the Al concentration is increased above to 0.389 moles, it is believed that the Al solubility in the cubic phase is exceeded and second phase  $LaAlO_3$  forms. It is suggested that Al substitutes for Li which creates charge compensating Li vacancies and it is these Li vacancies which determine phase stability.

At a fixed Al concentration to stabilize the cubic phase (0.240 moles) the effect of Li content was varied. It was found in all samples that there is Li loss heating at 1000 °C. At low Li contents (measured moles of Li = 5.63) cubic LLZO is present along with some second

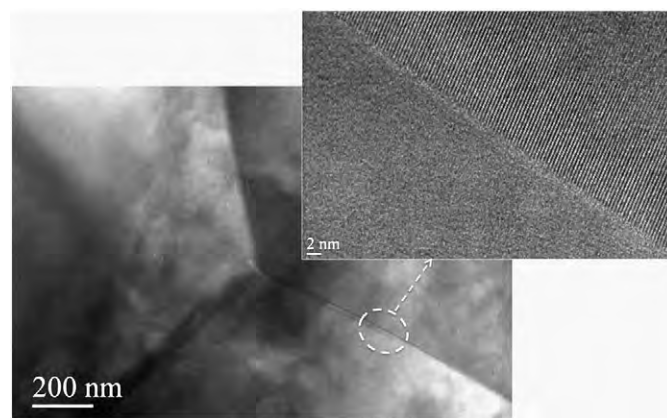


Fig. 5. TEM images of hot pressed  $Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}$ .

phase  $La_2Zr_2O_7$ . As the Li content increased from 5.63 to 6.24 moles only single phase cubic LLZO exists. As the Li content is further increased from 6.24 to 7.32 moles a transformation from cubic to tetragonal LLZO occurs. It is possible that the addition of Li above the critical Li concentration fills specific Li vacancy sites to the degree that one or more of the unit cell axes must distort to accommodate the further uptake of Li resulting in a non-cubic structure. From above, it is apparent that both Al and Li concentration play a critical role in the formation of cubic LLZO. Further work is required to determine how the ratio of Li to Al can be optimized to maximize ionic conductivity.

Based on the Al and Li results a pellet with an optimum concentration of Al (0.24 moles) and Li (6.24 moles) to form cubic LLZO was hot-pressed. The relative density of the hot-pressed material was 98%. The room temperature AC conductivity results for the hot-pressed cubic LLZO sample yields a total ionic conductivity value of  $4 \times 10^{-4} S/cm$ . The value of  $4 \times 10^{-4} S/cm$  is one of the highest values for the total ionic conductivity for cubic LLZO containing only Al with no other intentional additives. The electronic conductivity of the hot-pressed sample is  $2 \times 10^{-8} S/cm$ . The ionic transport number for cubic LLZO is equal to 1.0, confirming that cubic LLZO is an ionic conductor.

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